

The formation of nanopores in metal materials after irradiation by beams of Ar^+ with energy of 30 keV

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Abstract. In this paper are the results of direction observations of nanopores in the subsurface volume of metals materials Pt and Pd(CuAg) using field-ion microscopy (FIM). Radiation of tip specimens was carried out with ions having an energy $\sim 25\text{-}30$ keV in the fluency range of $10^{16} - 10^{18}$ ions/cm², the current density lying within $150\text{--}340$ $\mu\text{A}/\text{cm}^2$. Nanopores have been observed immediately after removal of the first atomic layers from the irradiated surface. It was established that, the threshold for ion-implanted platinum corresponds to fluence $F = 10^{17}$ ions/cm². For Pd(CuAg) it was revealed that nanopores have been down to 80 nm deep with current density 340 $\mu\text{A}/\text{cm}^2$. Their dimensions and volume fractions were determined. The obtained results can be used for prediction of radiation stability of materials based on fcc metals.

1. Introduction

Intensely developing studies of changes in the structure of metals and alloys after interaction between particle beams and the surface show that ionic treatment results in the formation of specific condensed states, as well as unique strength and physical properties in materials that cannot be obtained using conventional methods [1–6]. It was known that pore swelling in materials under irradiation causes shortening of the operational life of products and drastic deterioration of physical and mechanic properties of materials. Therefore, studies of the appearance of nanopores on the surface and in the subsurface layer of the studied objects under exposure to radiation on an atomic scale appear to be of current interest.

In this work, the results of modification of the surface and subsurface region of metals materials after irradiation by medium-energy charged particles (up to 30 keV) within a nanometer-deep surface region are shown. The method of field-ion microscopy (FIM) allows studying experimentally structural states appearing under such exposure. FIM allows directly visualizing and registering an atomically pure surface, analyzing the object of study in the subsurface region with the spatial resolution of the crystal lattice atoms and thus determining structural changes on the surface and in the subsurface region and various new states of the materials appearing under radiation exposure.

The aim of this work was to study experimentally (with atomic resolution) the phenomena of nanopore formation in metals materials after their interaction with charged beams of Ar^+ ions. In particular, it was intended to analyze the nanopore size distribution in the subsurface region as dependent on the distance from the irradiated surface and radiation fluence, determine the nanopore



formation threshold, and thus determine the optimum modes of radiation exposure to obtain nanostructured subsurface regions in ion-implanted metals and alloys.

2. Experimental

The objects of interaction with accelerated gas ion beams were pure metals (Pt) and constructional materials Pd (CuAg), used in special instrumentation for low-current contacts. Samples intended for study were prepared in the form of needle emitters with a tip curvature radius of 30–50 nm made of metal billets by electro polishing. The sample tips were evaluated using a field-ion microscope; i.e., an ion surface image of the corresponding materials in the initial state was obtained before their irradiation. Field emitters evaluated for ion implantation had an atomically smooth surface of the tip sample, close to a semispherical one. Such a surface was prepared by in situ field evaporation of the surface atoms.

Irradiation of needle samples (Pt) previously attested in a field ion microscope was carried out using gas ion (Ar^+) beams accelerated to 30 keV, with fluences $F = 3 \cdot 10^{16}$ to 10^{18} ion/cm² and ion current density $j = 150\text{--}200$ $\mu\text{A}/\text{cm}^2$, for Pd50Cu30Ag20 (wt%) - ion current density $j = 200\text{--}340$ $\mu\text{A}/\text{cm}^2$, with energy 25 keV. Bombardment was carried out in the direction parallel to the sample tip axis.

Implanted tip samples were again placed into an FIM, field ion surface micro patterns were registered using a photo or video camera with controlled removal of atomic layers, and changes in the structural state of bulk materials were analysed.

A field ion microscope was equipped with a micro channel ion–electron converter enhancing the brightness of surface micro images by 10^4 times. The refrigerant agent was generally liquid nitrogen ($T = 78$ K); the imaging gas was spectrally pure neon.

3. Results and discussion

Ion images of evaluated field emitters registered a regular ring pattern of the pure metal single crystal surface pointing to the virtual absence of structural defects (Fig. 1).

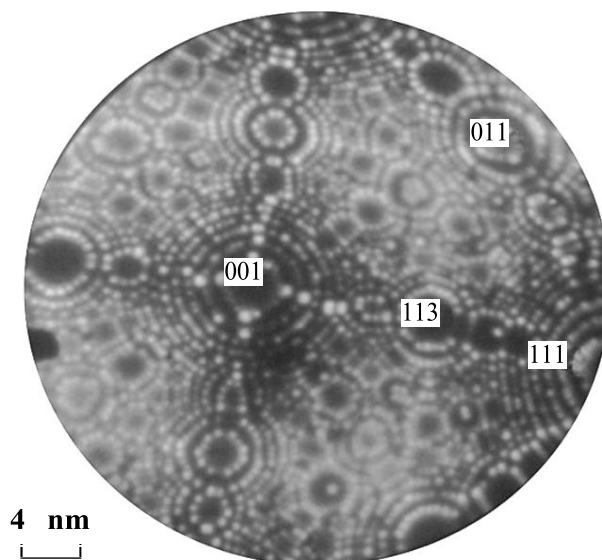


Figure 1. Neon image of validated Pt single crystal prepared for ionic irradiation.

In the microphotograph, faces {111}, {110}, and {113} are also registered, which are characteristic for crystals with an fcc lattice, in addition to the {001} face. The ring contour lines in ionic images are edges of the corresponding families of crystallographic planes of certain directions. Neighboring rings (from any family of concentric rings) are images of parallel atomic

layers. The rings themselves in an ionic micro image generally consist of separate bright points corresponding to images of surface atoms located at the sites of atoms in the step kinks.

In the course of studies of the crystalline structure of platinum irradiated to $F = 10^{16}$ to 10^{18} ion/cm² with an energy of 30 keV and $j = 200$ μ A/cm², ion contrast of nanopores was observed in the subsurface layer, apart from formation of nanosize blocks [4]. Such a contrast was observed at a fluence of 10^{17} ion/cm².

The contrast of nanopores in Pt was registered simultaneously with the appearance of an ionic image of the surface studied by FIM and was preserved after removal of several atomic layers of the implanted metal (Fig. 2a). Ion contrast of vacancy nanopores at the moment of field evaporation of the latter before the appearance of a nanopore of the atomic layer was registered in the form of a contrast of “craters.” Then, as the atomic layers around the defect evaporated, a vacancy cluster cross section with a size below that before the nanopore opening was observed. Finally, the nanopore outlet from the material in the course of the further evaporation of atomic layers from the surface generally ended in a dislocation loop (Fig. 2b).

The size of nanopores was estimated on the basis of the ionic contrast both using the area of the sample surface section by the defect measured on the basis of a calculation of the local surface radius on the face where the defect had appeared and by its depth via calculation of the number of evaporated atomic layers from the beginning of appearance of the nanopore contrast to its full disappearance. Results of quantitative analysis showed that nanopores had both spherical and cylindrical shapes. According to our estimates, their diameters were 1–5 nm. The size of nanopores across the depth was 1–9 nm. Successive evaporation of the surface atomic layers by electric field to the depth of 60 nm from the irradiated surface allowed elucidating specific regularities of nanopore formation. In particular, information could be obtained on the nanopore concentration and their distribution in the subsurface layer of the irradiated material. As a result, it was found that up to 40% of the pores were concentrated in the subsurface layer with a thickness of 10 nm. Later, the bulk fraction of nanopores decreased logarithmically (Fig. 3). As is known from [7], argon atoms in the case of applied beam energies have a projective path in platinum not above 10 nm.

It is, hence, obvious that threshold swelling in the material was not related to the presence of implanted argon ions in the defects, as nanopores were observed in the metal up to the depth of 60 nm.

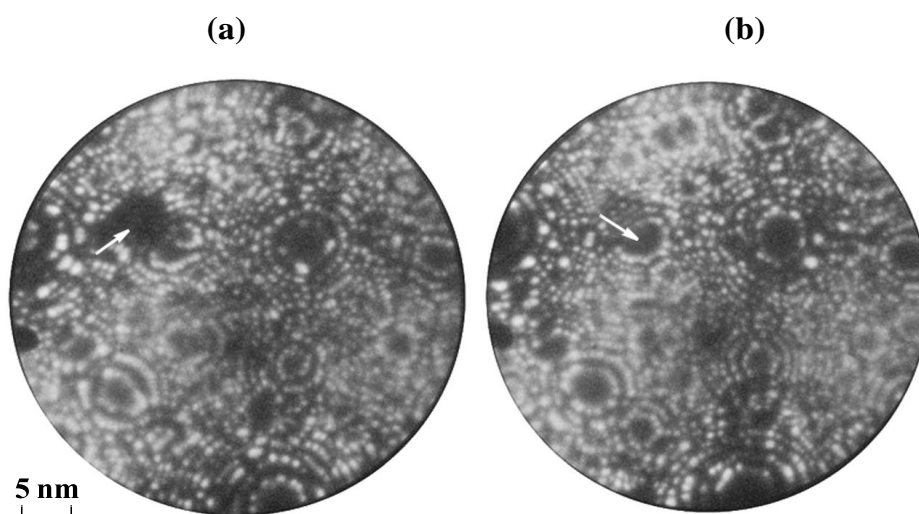


Figure 2. Neon images of pure Pt after irradiation by Ar⁺ ions ($E = 30$ keV, $F = 10^{17}$ ion/cm²): (a) typical ionic contrast of a vacancy nanopore (shown by an arrow); (b) contrast of a dislocation loop at the nanopore outlet from the material after field evaporation of 8 atomic layers with respect to the (001) face (~ 1.6 mm) (shown by an arrow).

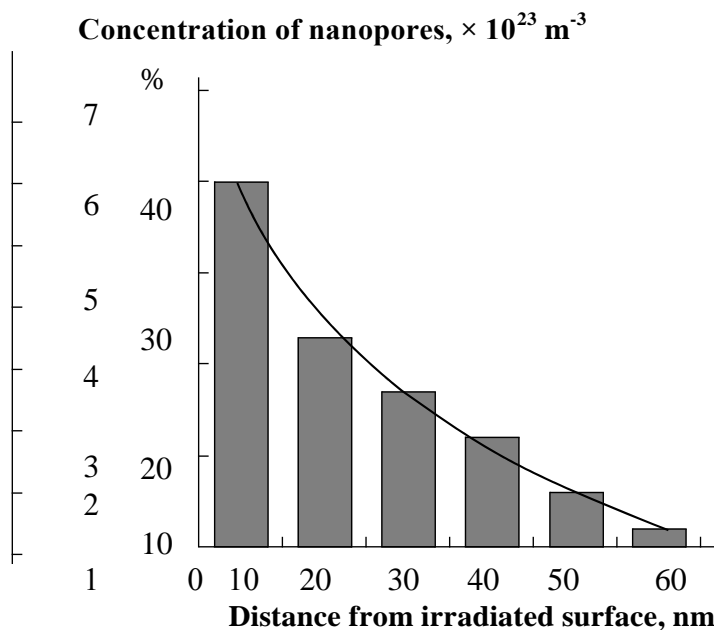


Figure 3. Concentration of nanopores in platinum irradiated by Ar^+ ions ($F = 10^{18} \text{ ion/cm}^2$).

Detailed analysis of experimental data allowed assuming that ion implantation resulted in continuous appearance and migration of implanted atoms and vacancies to drains and coalescence of individual vacancies into vacancy nanoclusters (nanopores).

As a result of argon ion implantation ($E = 25 \text{ keV}$, $j = 340 \text{ } \mu\text{A/cm}^2$, $F = 10^{18} \text{ ions/cm}^2$) the structural state of ternary solid solution $\text{Pd}(\text{CuAg})$, Fig. 4a [8], changed. This being clearly evident from Fig. 4b, which reveals an atomically clean surface of the irradiated alloy. The micrograph shows a superstructural (001) pole of a particle of the PdCu ordered B2 phase [8].

The examination of the subsurface volume of the said alloy in the course of the field evaporation of atoms of the material itself revealed an ion contrast similar to that due to nanopores and found [9]. The said contrast appeared as crater after the first surface layer of the irradiated solid solution had evaporated. Fig. 5 shows a typical example of such contrast. Quantitative analysis has shown that the nanopores were ellipsoidal in shape. According to our estimates their diameters were within 3-12 nm and their depth within 4-25 nm. The ratio of nanopores volume to that of the materials analysed, wherein the pores were found, was assessed on the basis of quantitative measurements of the size and the number of vacancy clusters in the subsurface volume of the irradiated alloy. Fig. 5 illustrates the spatial disposition of nanopores in the subsurface volume. Analysis has shown that the volume fraction of vacancy clusters decreases monotonically with the depth of occurrence of defects (Fig. 6).

According to our estimates the maximum depth of the occurrence of nanopores after irradiation with $j = 340 \text{ } \mu\text{A/cm}^2$, based on the calculation of the evaporated atomic layers, was found to be ca 80 nm and this is referred to the irradiated surface. With the decrease of the irradiation current density down $300 \text{ } \mu\text{A/cm}^2$ the depth of occurrence of nanopores dropped to 17 nm. At the same time it is known [7] that argon ions at the energies used here. Are implanted into pure components comprising of the alloy down to a depth $\leq 15 \text{ nm}$.

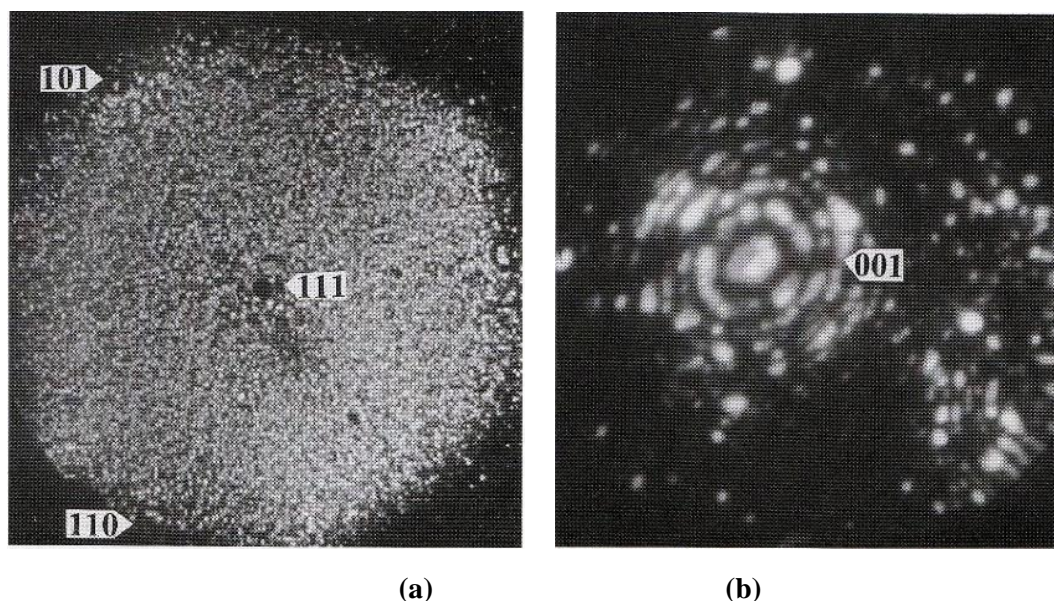


Figure 4. (a) Micrograph of Pd(CuAg) solid solution surface certified in FIM just before irradiation (annealing at 1123 K for 1 h and water quenching); (b) micrograph of the Pd(Cu) ordered phase particle following ion implantation.

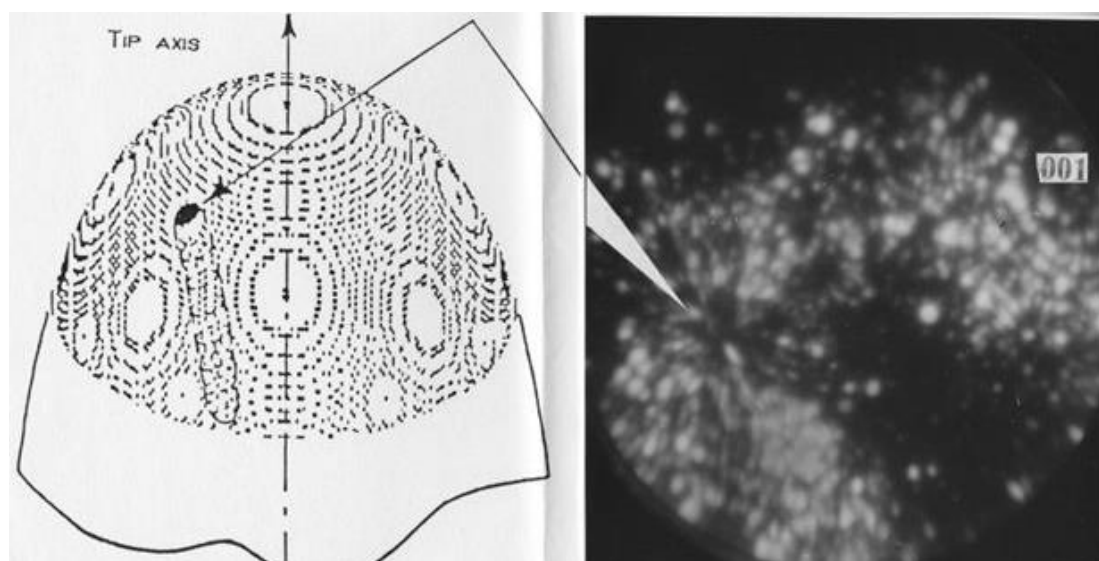


Figure 5. Schematic representation of the spatial disposition of the nanopores in the subsurface volume of the Pd(CuAg) specimen and typical ion contrast of nanopores in Pd(CuAg) after irradiation.

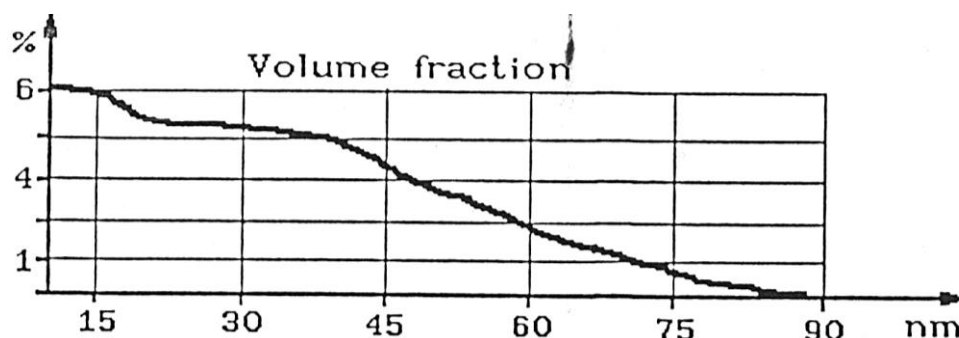


Figure 6. The variation of the volume fraction of nanopores with the depth of an irradiated Pd(CuAg) specimen in the subsurface layers ($E = 25$ keV, $j = 340 \mu\text{A}/\text{cm}^2$, $F = 10^{18}$ ions/ cm^2).

4. Conclusion

Thus, an experimental study of nanopore formation both on the surface and in the subsurface metal materials bulk within a nanometer range from the irradiated surface was carried out on the atomic scale.

Ion implantation modes at which nanopore formation started were determined. For pure metals (Pt), nanopores appeared at fluences of $10^{17} - 10^{18}$ ion/ cm^2 in the energy range of 20–30 keV, starting from $j = 200 \mu\text{A}/\text{cm}^2$. The distribution and bulk fraction of nanopores in the subsurface material bulk were studied. As a result, it was found that up to 40% of the pores were concentrated in the subsurface layer with a thickness of 10 nm. Later, the bulk fraction of nanopores decreased logarithmically.

The FIM technique has been used to detect porous swelling in the subsurface volume of Pd(CuAg) alloy irradiated with low-energy ($E = 25$ keV) argon ions. This swelling is due to radiation-induced precipitation break-up taking place in the solid solution. It was established that nanopores are elliptical in shape with diameters within 3 – 12 and height within 4 – 25 nm.

The obtained results can be used for prediction of radiation stability of materials based on fcc metals.

Acknowledgements

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